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Dye-sensitized Photolysis of Diazonium Compounds in the Presence of Thioacetamide

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Synposis. Effects of solution pH and molecular oxygen on the quantum yields of methylene blue-sensitized photolysis of diazonium salt have been studied in aqueous solutions, using thioacetamide as an activator. The quantum yield increased with an increase in pH when other parameters were kept constant. The presence of oxygen at pH (<7) promoted dye sensitization, but at pH (>7) dominance of the pathway of oxygen quenching of the excited dye triplet caused its suppression. The polymerization of acrylamide in the deaerated solution was readily initiated by dye-sensitized photolysis. A mechanism involving an electron transfer to diazonium cation from unprotonated semimethylene blue formed by a photoredox reaction between excited triplet dye and thioacetamide was in line with these observation.

The methylene blue (MB) sensitized photolysis of 4-diazodiphenylamine sulfate (4DS) solutions containing sodium *p*-toluenesulfinate (STS) or 1,4-diazabicyclo-[2,2,2]octane (DABCO) as an activator was studied by flash photolysis and continuous illumination.[1,2] The mechanism of photolysis was shown to be an electron transfer (see the simplified reaction scheme).

$$\mathrm{MB^{+*} + STS \rightarrow MB\cdot\text{---}\cdot STS \xrightarrow{O_2} MB\cdot + STS\text{-}O_2\cdot} \quad (1)$$

$$\mathrm{MB^{+*} + DABCO \rightarrow MB\cdot\text{---}\cdot DABCO \rightarrow MB\cdot + DABCO\cdot} \quad (2)$$

$$\mathrm{MB\cdot + 4DS \rightarrow MB^{+} + diphenylamine\ radical + N_2} \quad (3)$$

Here the primary reaction takes place between MB triplet ($\mathrm{MB^{+*}}$) and STS or DABCO (called "activator") with the formation of a complex consisting of a semi-MB (MB·) and a half-oxidized activator radical (sulfonyl radical or DABCO cation radical). In the STS system, oxygen was necessary for the dye sensitization at pH below 7. This could be explained in terms of an attack of oxygen on the sulfonyl radical component in a complex, which caused the escape of a semi-MB from the complex (the second step of reaction (1)). The semi-MB was considered to decompose 4DS according to (3). In the absence of oxygen, the complex reverted rapidly to MB and STS in the ground state. The quantum yield markedly decreases if low concentration of STS is chosen for fulfilling the dominance of the pathway of oxygen quenching of triplet MB.[3] The suppression of dye sensitization by oxygen indicates that oxygen quenches triplet MB. In order to understand the operation of dye-sensitized diazo systems, it is important to study a dye-sensitizing system containing other activators such as thioacetamide. Using MB, 4DS and thioacetamide (TAA) which act as an activator, effects of solution pH and oxygen on the quantum yield of MB-sensitized photolysis of 4DS were studied. All the experiments were performed at room temperature 23±1 °C. The solutions were degassed to 10^{-4} mm Hg by the usual freeze-pump-thaw cycle. Experimental procedures were the same as those described previously.[1,2] Oxygen concentrations in aqueous solutions under various partial pressures of oxygen gas were calculated by use of Bunsen's absorption coefficient 0.03 (at 23 °C).[4] Figure 1 shows the absorption spectra of the aerobic solution containing 2.0×10^{-5}M MB, 5.0×10^{-3}M thioacetamide (TAA) and 4.0×10^{-5} M 4DS at pH 6.0 before and after irradiation. Photo-excitation of MB brought about the sensitized photolysis of 4DS as represented by the decrease of an absorption maximum of 4DS at 380 nm. 4DS was stable in the dark at pH lower than 8.4. In the absence of TAA no significant sensitization occurred. The presence of oxygen at pH 6.0 promotes dye sensitization, since quantum yields were about 0.13, and 0.05 for the aerobic and deaerated systems containing 2.0×10^{-5} M MB, 5.0×10^{-3} M TAA, and 4.0×10^{-5} M 4DS at pH 6.0, respectively. Oxygen effect on

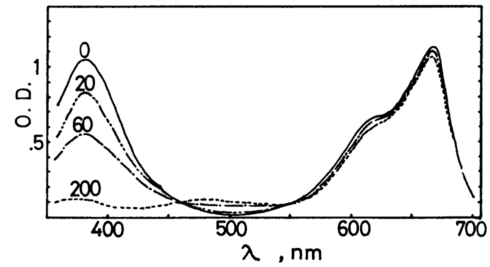


Fig. 1. Absorption spectra of 4DS solutions containing MB and TAA under an aerobic condition.
Numbers indicate the irradiation time (s) of red light (2.1×10^{-6} Einstein absorbed/l·s). Cell thickness is 1 cm. $[\mathrm{4DS}]=4.0\times10^{-5}$ M, $[\mathrm{TAA}]=5.0\times10^{-3}$ M, $[\mathrm{MB}]=2.0\times10^{-5}$ M, pH 6.0.

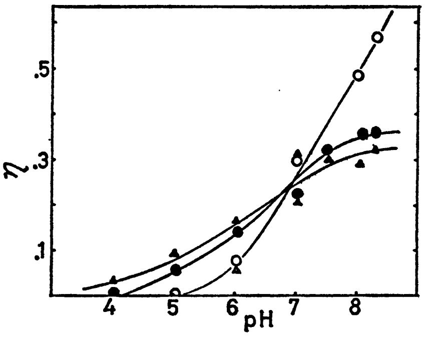


Fig. 2. Dependence of quantum yields (η) on solution pH $[\mathrm{4DS}]=3.8\text{—}4.2\times10^{-5}$ M, $[\mathrm{TAA}]=5.0\times10^{-3}$ M, $[\mathrm{MB}]=2.0\times10^{-5}$ M, ○: $\mathrm{N_2}$-bubbled, ●: aerobic, △: deaerated, ▲: $\mathrm{O_2}$-bubbled.

quantum yields of dye-sensitized photolysis of 4DS is shown for the deaerated, N_2-bubbled, aerobic, and O_2-bubbled solutions, together with pH effect in Fig. 2. In the deaerated, N_2-bubbled, aerobic and O_2-bubbled systems, oxygen concentrations were taken to be $\sim 10^{-11}$ M, $\sim 10^{-9}$ M, 3×10^{-4} M, and $1 \sim 2 \times 10^{-3}$ M, respectively. The quantum yield in all systems increased with an increase in pH. It increased with an increase in oxygen concentration at pH below 7, whereas the reverse was the case at pH above 7.

In the deaerated system containing 1M acrylamide, MB excitation efficiently induced the free radical polymerization of acrylamide accompanied by sensitized photolysis of 4DS. The pH dependence of monomer conversion and the amount of MB bleached and 4DS decomposed under the exposure to the red light for 15 s is shown in Fig. 3. The rates of the sensitized photolysis and polymerization increased with an increase in pH. The molecular weights of polymers were of the order of millions. No significant polymerization of acrylamide was observed in the absence of 4DS or TAA. The results suggest that the photopolymerization of acrylamide in the deaerated TAA system is initiated by diphenylamine radical formed *via* an electron transfer from semi-MB to 4DS as reported for STS or DABCO systems.[2] At higher pH where the sensitized photolysis of 4DS was observed, a greater part of the MB triplet should be in an unprotonated form, since pK_a of protonated MB-triplet was 6.7.[5] Thus, little MB bleaching during polymerization can be explained in terms of an electron transfer causing the regeneration of MB^+ (reaction 3).

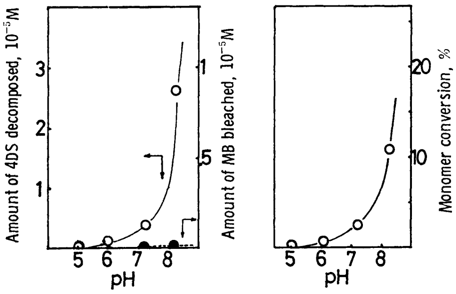
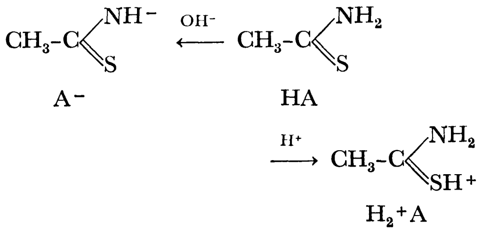


Fig. 3. Effect of solution pH on the sensitized photolysis of 4DS, MB photo-bleaching, and monomer conversion.
Intensity of red light: 2.2×10^{-6} Einstein absorbed/l·s. $[MB]_{ini} = 2.0 \times 10^{-5}$ M, $[TAA]_{ini} = 5.0 \times 10^{-3}$ M, $[4DS]_{ini} = 3.8$—4.0×10^{-5} M, $[Acrylamide]_{ini} = 1$ M, Irradiation time: 15 s.

At pH above 7, oxygen suppression of the dye-sensitized photolysis of 4DS might be related to a quenching mechanism of triplet MB such as singlet oxygen mechanism.[3] If oxygen quenching of triplet MB or semi-MB alone is taken into account, oxygen effect on quantum yield at a pH less than 7 should be similar to that at a pH above 7. However, oxygen at pH (<7) promoted dye sensitization (Fig. 2). When aerobic aqueous solutions containing 2.0×10^{-5} M MB and 5.0×10^{-3} M TAA in the pH region $5 \sim 9$ were exposed to red light, the dissolved oxygen was consumed by TAA. According to studies of thionine-sensitized photooxygenation of allylthiourea by Kramer and Maute,[6] the primary reaction takes place between thionine triplet and allylthiourea accompanied by the formation of semithionine radical and allylthiourea cation radical. Oxygen is involved only after the radicals have been formed.

The effectiveness of dissolved oxygen at pH (<7) suggests a mechanism in which molecular oxygen reacts with a charge-transfer complex formed between triplet MB and TAA to form semi-MB effective for dye sensitization, and which was disscussed for the STS system.[2] An attempt to check the above possibility by flash photolysis (400 J, 20 μsec) was unsuccessful since the amount of transient MB-bleaching observed in solutions containing MB and TAA was too small to measure the effect of oxygen or 4DS on the transient bleaching. The spectral changes of TAA in more alkaline or acidic solutions are attributed to the reaction:[7]



$$\underset{\mathrm{A^-}}{\mathrm{CH_3{-}C}\begin{smallmatrix}\mathrm{NH^-}\\ \mathrm{S}\end{smallmatrix}} \xleftarrow{\mathrm{OH^-}} \underset{\mathrm{HA}}{\mathrm{CH_3{-}C}\begin{smallmatrix}\mathrm{NH_2}\\ \mathrm{S}\end{smallmatrix}} \xrightarrow{\mathrm{H^+}} \underset{\mathrm{H_2^+A}}{\mathrm{CH_3{-}C}\begin{smallmatrix}\mathrm{NH_2}\\ \mathrm{SH^+}\end{smallmatrix}} \qquad (4)$$

TAA is neutral in the pH region we worked with, since pK_a's of HA and H_2^+A are 13.4 and -1.9, respectively. The pK_a of H_2^+A was determined from a relationship ($[HA]/[H_2^+A] = K_a/h_+$) between $[HA]/[H_2^+A]$ and acidity function ($H_+ = -\log h_+$) in sulfuric acid solutions. Thus, it seems unreasonable that a loss of electron donating power derived from a protonation of TAA brought about a decrease in the quantum yield at lower pH. The space cause of the difference in quantum yield with different pH is unknown.

References

1) T. Yamase, T. Ikawa, H. Kokado and E. Inoue, *Photogr. Sci. Eng.*, **17**, 28 (1973).

2) T. Yamase, T. Ikawa, H. Kokado and E. Inoue, *ibid.*, **17**, 268 (1973).

3) C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968).

4) G. Brauer, "Handbuch der präparativen anorganischen Chemie," Stuttgart (1954), p. 352.

5) S. Kato, M. Morita, and M. Koizumi, This Bulletin, **37**, 117 (1964).

6) H. E. A. Kramer and A. Maute, *Photochem. Photobiol.*, **15**, 7, 25 (1972).

7) J. T. Edward and I. C. Wang, *Can. J. Chem.* **40**, 399 (1962).